

**Seeing many-body effects in single- and few-layer graphene:
Observation of two-dimensional saddle-point excitons**

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Significant excitonic effects were observed in graphene by measuring its optical conductivity in a broad spectral range including the two-dimensional π -band saddle-point singularities in the electronic structure. The strong electron-hole interactions manifest themselves in an asymmetric resonance peaked at 4.62 eV, which is red-shifted by nearly 600 meV from the value predicted by *ab-initio* GW calculations for the band-to-band transitions. The observed excitonic resonance is explained within a phenomenological model as a Fano interference of a strongly coupled excitonic state and a band continuum. Our experiment also showed a weak dependence of the excitonic resonance in few-layer graphene on layer thickness. This result reflects the effective cancellation of the increasingly screened repulsive electron-electron (*e-e*) and attractive electron-hole (*e-h*) interactions.

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A fundamental issue in understanding the unique properties of electrons in graphene, a single layer of carbon atoms, is the role of many-body interactions in this system. Many-body interactions are generally more significant in two-dimensional (2D) materials than in their bulk counterparts. This reflects both the intrinsic enhancement of the importance of Coulomb interactions in 2D materials, as well as their reduced screening. Indeed, the behavior of low-energy quasiparticles in graphene is significantly altered by electron-electron interactions, as manifested by recent reports of broken symmetry states in the quantum Hall regime [1], of the fractional quantum Hall effect [2], of a renormalization of the Fermi velocity [3], and of plasmarons [4]. The role of electron-hole interactions, as are relevant for the optical response, has remained somewhat paradoxical. On the one hand, theoretical studies have predicted strong excitonic corrections to the optical response [5-9], as well as BCS superfluidity at high quasiparticle density [10] and magnetoexcitonic superfluidity under high magnetic fields [11]; on the other hand, the vast preponderance of experimental data, including the optical conductivity in the infrared, can be understood within an independent-particle description of carriers in linearly dispersing bands [12-16].

In this Letter, we present direct experimental evidence of large excitonic corrections to the optical response of graphene. We do so by measuring graphene's optical conductivity over a wide range of photon energies (0.2 – 5.3 eV). Above the infrared spectral range, we observe that the optical conductivity starts to deviate significantly from the universal value of $\pi e^2/2h$ predicted within an independent-particle model [17] and demonstrated experimentally [15, 16]. A pronounced resonance feature arises in the ultraviolet from transitions near the *M*-point, a saddle-point van Hove singularity, of the Brillouin zone of graphene [18]. The feature is well known in graphite [19] and has recently been observed in graphene [20]. While the enhanced absorption associated with this feature is expected within an independent-particle picture, the marked asymmetry of the line shape cannot be understood [21]. Further, the measured position of the peak, when compared with theory, also indicates a large shift (~ 600 meV) to lower energies from excitonic interactions [7]. We attribute these features to strong electron-hole (*e-h*) interactions of the quasiparticles near the 2D saddle-point singularity. The distinctive asymmetric line shape can be viewed as an interference effect in the classic theory of Fano [22, 23] for a discrete state residing within a continuum. The detailed spectral dependence of this excitonic resonance is found to be in excellent agreement with the result of recent first-principles calculations [7]. In addition, only a very slight variation of excitonic resonance with layer thickness was observed in few-layer graphene (FLG), despite the increased screening of the Coulomb interaction for thicker samples. This weak dependence on screening reflects the effective cancellation of the repulsive *e-e* interactions, which shift the transition upwards in energy, and the attractive *e-h* interactions, which shift it downwards [7].

In our measurements, we made use of graphene samples prepared by mechanical exfoliation of kish graphite (Toshiba) on SiO₂ substrates (Chemglass). The procedure for sample preparation and characterization is described in [16, 24, 25]. The optical response was determined using different sources for different wavelength regimes. For the mid-to-near IR range (0.2 – 1.2 eV) radiation from the National Synchrotron Light Source at Brookhaven National Laboratory was employed together with a Fourier-transform infrared microscope [16, 24]. The visible (1.5 – 3.0 eV) and UV (3.0 – 5.3 eV) ranges

were examined in our laboratory with, respectively, a quartz tungsten halogen (QTH) and a deuterium source, coupled with a confocal microscope. A reflective objective was employed in the UV range to enhance the throughput. The visible/UV beam was focused onto the sample with a spot size of $2 - 3 \mu\text{m}$ diameter, and the reflected beam was analyzed with a grating spectrometer and a UV-enhanced CCD camera.

We obtain the optical conductivity of graphene directly from the reflectance contrast $\Delta R/R$, the normalized change in reflectance of the bare substrate induced by the presence of the sample. For a sufficiently thin sample supported on a transparent substrate with refractive index n_s , the optical sheet conductivity, $\sigma(E)$, at photon energy E

is given by $\sigma(E) = \frac{c}{4\pi} \frac{n_s^2 - 1}{4} \frac{\Delta R}{R}$ [16]. For the spectral window of our measurements, the

SiO_2 substrate has negligible absorption and the dispersion of n_s has been well established [26]. The thin sample approximation also holds reasonably well for graphene thickness up to 5 layers [24]. Thus, we were able to obtain the optical conductivity (or, equivalently, absorption) spectrum of graphene samples directly from their reflectance contrast spectrum.

The measured optical conductivity spectrum $\sigma(E)$ for a graphene monolayer (Fig. 1) displays several noteworthy features. (i) In the near-IR spectral range of $0.5 - 1.5 \text{ eV}$, $\sigma(E)$ is described well by the universal value of $\sigma = \pi e^2/2h$, as derived previously within the independent-particle theory [17] and confirmed experimentally [15, 16]. (ii) In the visible spectral range, $\sigma(E)$ rises smoothly and steadily, increasing by $\sim 80\%$ at 3.0 eV . (iii) In the UV range, $\sigma(E)$ displays a pronounced peak at $E_{\text{exp}} = 4.62 \text{ eV}$. In the independent-particle description, this feature arises from interband transitions in graphene from the bonding to the antibonding π -states near the saddle-point singularity at the M -point of the Brillouin zone [18]. GW calculations, which are known to be accurate in describing the quasiparticle bands of graphene (but ignore the e - h interactions), predict a band-to-band transition energy of $E_{\text{GW}} = 5.2 \text{ eV}$ at the M -point [Fig. 2(b)] [7, 27]. The observed peak energy E_{exp} is red-shifted from E_{GW} by almost 600 meV , over 10% of the saddle-point energy. (iv) The observed resonance feature has an asymmetric line shape, with higher optical conductivities on the low photon energy side. Such an asymmetry is also in disagreement with the single-particle description. In this description, the optical transition matrix elements depend only weakly on the energy E in the vicinity of the 2D saddle-point singularity. The spectral dependence of the optical conductivity is then governed by the joint density of states (JDOS), $-\log |1-E/E_0|$ [21], which is symmetric in energy about the saddle point energy E_0 .

A natural way to account for the observed discrepancies from the independent-particle description of the optical response of graphene is to include e - h interactions. Effects of the e - h interaction near saddle-point singularities have been extensively investigated theoretically [28]. This interaction gives rise to significant changes in the line shape near the saddle point. This redistribution of oscillator strength can be understood in terms of the development of discrete excitonic states below the saddle-point singularity from the attractive e - h interactions. Meanwhile, since the constant energy surface near a saddle point is a hyperboloid, there is also a continuum of allowed states with energy below the saddle point. These states strongly couple and often lead to asymmetric resonance features with higher conductivities on the low-energy side [23, 28, 29]. Philips [23] has interpreted these resonances in terms of a Fano interference [22, 23]

between discrete states and the continuum. We extend this phenomenological approach to graphene by including a single dominant excitonic state. We express the resultant optical conductivity $\sigma(E)$ as:

$$\frac{\sigma(E)}{\sigma_{cont}(E)} = \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}. \quad (1)$$

Here $\sigma_{cont}(E)$ denotes the optical conductivity arising from the unperturbed band-to-band transitions (*i.e.*, without e - h interactions); $\varepsilon = (E - E_{res}) / (\Gamma / 2)$ is the energy relative to the resonance energy E_{res} of the perturbed exciton (*i.e.*, with coupling to the continuum) and normalized to width Γ . The parameter q^2 defines the ratio of the strength of the excitonic transition to the unperturbed band transitions, while the sign of q determines the asymmetry of the line shape arising from interference effect.

The behavior predicted by the phenomenological Fano model is shown in Fig. 2(a). We model the unperturbed band transitions by the JDOS near the saddle-point singularity, $\sigma_{cont}(E) \sim -\log |1 - E/E_0|$, broadened by convolution with a Lorentzian of width $0.01E_0$ to account for broadening from carrier relaxation. For the appropriate Fano parameters ($q = -1$, $E_{res} = 0.95E_0$, $\Gamma = 0.01E_0$), we obtain a spectrum with a peak red-shifted from E_0 and an asymmetric line shape with enhanced optical conductivity on the low-energy side. Despite its simplicity, we see that this model captures the main features of the experimental optical conductivity spectrum. A more quantitative analysis can be carried out using the results of published GW calculations for the continuum background [7], which provides a better description of the response well away from the singularity. We consequently take $\sigma_{cont}(E) = \sigma_{GW}(E)$, where we have convoluted the theoretical results with broadening of 250 meV to reflect the experimentally observed width. The best fit to Eq. 1 then yields $q = -1$, $E_{res} = 5.02$ eV, and $\Gamma = 780$ meV. The exciton resonance energy is seen to be red-shifted by 180 meV from the GW peak at $E_{GW} = 5.20$ eV. The large value of the width parameter Γ corresponds to an exciton lifetime of only ~ 0.5 fs, indicating a very high rate of autoionization of the excitonic state into the continuum. We also compare the experimental spectrum to the recent result of full *ab-initio* calculations in which excitonic effects were taken into account using the GW-Bethe-Salpeter approach (GWBS) [7] [dashed line of Fig. 2(b), broadened by 250 meV]. Both the GWBS calculations and the phenomenological model provide excellent agreement with the available experimental data.

Although the effects of e - h interactions near a saddle point are known to be significant in insulators and semiconductors [28], the observed excitonic effects in graphene must be considered in terms of the dielectric response of a semimetal. In a highly conductive system like graphene, one might expect effective screening of the Coulomb potential and, consequently, weak e - h interactions. Indeed, theoretical investigations have shown that screening of charges in the 2D graphene system arises from a combination of “metallic” screening by intraband transitions and “insulating” screening from interband transitions [30]. The former is similar to screening in other 2D electron systems, but the relatively low DOS near the Dirac point, a consequence of the linear dispersion relation, reduces this contribution compared to that which would be present in a normal metal. In addition, the effectiveness of all screening processes in graphene is diminished by the fact that the charges can act upon one another with electric field lines that penetrate into the surrounding media, which usually exhibit a weaker

dielectric response. As a consequence of these effects, the Coulomb interaction remains quite effective in graphene and accounts for the pronounced excitonic corrections that we see experimentally.

How does the excitonic resonance vary with layer thickness N in FLG? While the band structure near the M-point is modified by interlayer interactions [27, 31], because of the symmetry properties of the electronic states, only optical transitions with very similar energies are dipole allowed. Thus, the band structure changes are not expected to lead to a significant shift in the optical resonance, as shown below [32]. On the other hand, we expect that the screening of the e - h interactions will become considerably more effective as the thickness of the sample increases towards the bulk limit. Stronger screening is expected both from the enhanced dielectric constant of the surrounding environment of each layer and from the increased density of states at the Fermi energy [31]. Thus, excitonic effects are expected to diminish with increasing layer number. In fact, however, only very slight changes in the excitonic resonance were observed in our experiment for $N = 1 - 5$ layers [Fig. 3(a)]. The optical conductivity increases almost linearly with layer thickness, except a small red shift of the resonance peak E_{exp} [Fig. 3(b)].

To understand this unexpected behavior of the excitonic resonance in FLG, let us examine the peak positions calculated within several *ab-initio* approaches to the electronic structure: E_{LDA} from the density-functional theory (DFT) in the local-density approximation [32], E_{GW} from the GW corrections to DFT [7], and E_{GWBS} from the GW-Bethe-Salpeter treatment [7]. E_{LDA} underestimates the peak energy E_{exp} , but like the experimental data depends very weakly on N . The lack of a dependence on layer thickness and the associated screening reflects the omission of both long range e - e correlations and e - h interactions [27]. It also shows that band structure changes of the material, as a result of interlayer interactions, do not lead to a significant change in the resonance energy. On the other hand, E_{GW} overestimates the peak energy and shifts to lower energies with increasing N . This behavior arises from the inclusion of the e - e repulsion (but not e - h attraction), with improved screening of the e - e repulsion with increasing layer thickness. Indeed, the peak energy converges rapidly to the bulk (graphite) value for layer thickness $N > 3$. Now with both e - e and e - h interactions taken into account within the GW-Bethe-Salpeter approach, we see that E_{GWBS} agrees well with experiment. The peak positions display only a slight red shift with increasing N . Thus, the weak dependence of the excitonic resonance energy on N observed experimentally is not the consequence of identical screening of Coulomb interactions for different N . It is rather a result of a significant cancellation of comparable repulsive and attractive Coulomb interactions. The net energy of the excitonic state is thus less sensitive to screening than that of either the quasiparticle band gap or the exciton binding energy taken alone. The phenomenon is analogous to the optical transitions observed/predicted in carbon nanotubes [33-37] and graphene nanoribbons [5].

In conclusion, our experiment has provided the first direct evidence of strong excitonic effects in the optical response of graphene. The optical resonance associated with the van Hove singularity at the M-point is significantly modified because of the e - h interactions, and an asymmetric and shifted excitonic feature develops. In addition to its intrinsic interest, graphene is an excellent model system for the study of 2D saddle-point excitons. We have qualitatively described the excitonic resonance in graphene within the phenomenological Fano theory as an interference of a discrete excitonic state and the

band continuum. Further refinement of this model is clearly warranted, as is testing of its applicability for varying conditions. Of particular interest would be probing of the excitonic response at variable doping density.

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Figures:

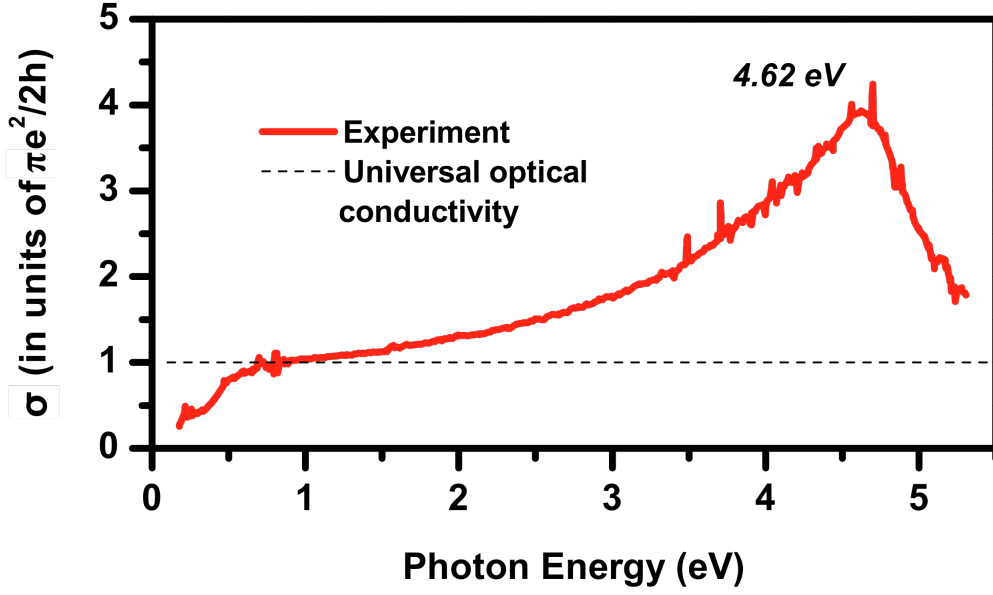


Figure 1: Experimental optical conductivity (solid line) and the universal optical conductivity (dashed line) of monolayer graphene in the spectral range of 0.2 – 5.5 eV. The experimental peak energy is 4.62 eV. Note the deviation of the optical conductivity from the universal value at low energies is attributed to spontaneous doping [16].

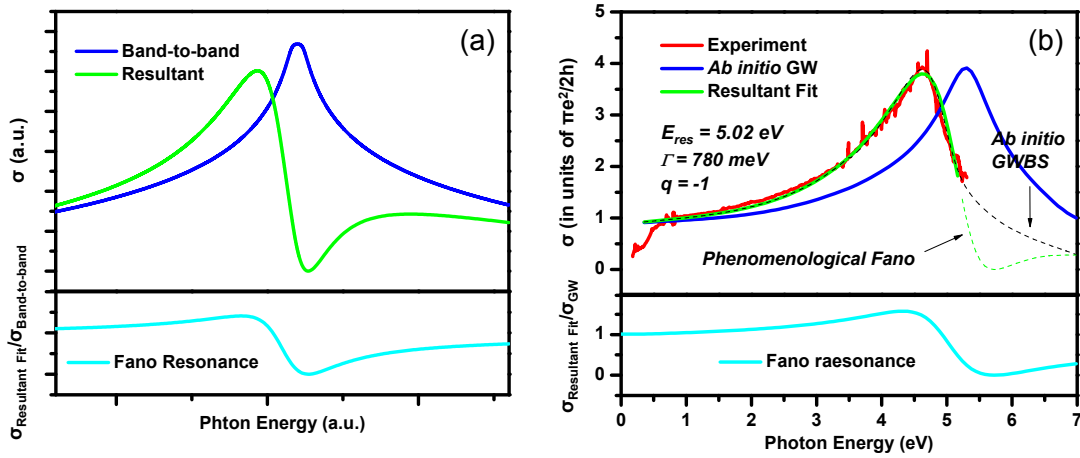


Figure 2: Fano theory of saddle-point excitons in graphene. Upper panels: optical conductivity of unperturbed band-to-band transitions σ_{cont} (blue) and the resultant conductivity from a Fano interference of the exciton state and the continuum (green); lower panels: Fano line shape of Eq. 1. (a) Illustration of the model using the JDOS near the 2D saddle point for σ_{cont} and the Fano parameters as described in the text. (b) Fit of experiment (red) to the Fano model using the optical conductivity obtained from GW

calculations [7] for σ_{cont} . The dashed line is the optical conductivity spectrum obtained from the full GW-Bethe-Salpeter calculation [7].

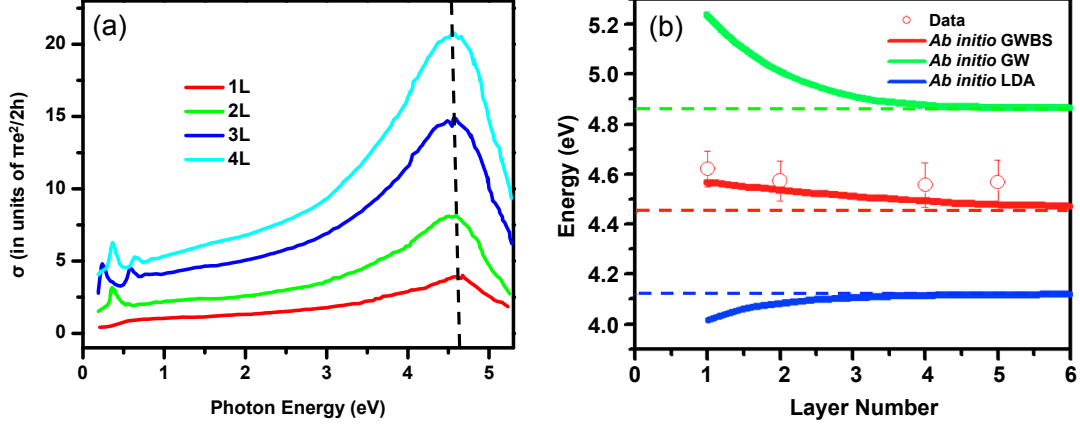


Figure 3: (a) Experimental measurement of the optical conductivity for single- and few-layer graphene in the spectral range of 0.2 – 5.3 eV. The vertical dashed line is a guide to the eye in the region of the excitonic resonance. (b) Dependence of the peak energy of the excitonic resonance on layer thickness: experiment (symbols), values calculated from *ab initio* LDA (blue), GW (green) and GWBS (red). The dashed lines show the calculated value for bulk graphite.

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